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Vapor Trace® Shallow Soil Gas and Groundwater Investigation

Plummer Quik Stop Plummer, Idaho

February 8, 1995

Site assessment performed for PSTF underwriting and insurance purposes only. No other use of results authorized by PSTF.



### 1.0 INTRODUCTION

Tracer Research Corporation (Tracer Research) performed a shallow soil gas and groundwater investigation at IPSTF Site #1430-5-2, Plummer Quik Stop, in Plummer, Idaho. The investigation was conducted February 8, 1995, for the Idaho Petroleum Storage Tank Fund (IPSTF). The purpose of the investigation was to assess the potential presence of petroleum hydrocarbons in the vicinity of three underground storage tanks (USTs), one aboveground storage tank (AST) and associated piping located on site.

Fourteen soil gas and five groundwater samples were collected and analyzed from twelve sampling locations. Samples were analyzed for the following petroleum hydrocarbons:

COMPOUND	DETECTOR
benzene	FID
toluene	FID
ethylbenzene	FID
xylenes	FID
total volatile hydrocarbons	FID

The total of the three xylene isomers are simply reported as xylenes. Gasoline range compounds, consisting of approximately  $C_1$ - $C_9$  aliphatic, alicyclic, and aromatic compounds, are reported as total volatile hydrocarbons (TVHC).

The compounds in this suite were chosen as target compounds because of their presence in petroleum fuels stored on site, their suspected presence in the subsurface and their amenability to soil gas technology. The samples were screened on a gas chromatograph (GC) equipped with a flame ionization detector (FID).

## 2.0 SHALLOW SOIL GAS INVESTIGATION - METHODOLOGY

Tracer Research has developed a method for investigating underground contamination from Volatile Organic Compounds (VOCs), such as industrial solvents, cleaning fluids, and petroleum products. This method looks for VOC vapors in the shallow soil gas.

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A hollow probe is driven into the ground and a small amount of soil gas is pulled by vacuum into the probe. A hypodermic needle is inserted into an evacuation line in the probe and the soil gas is extracted into a glass syringe. The soil gas from the syringe is injected into a GC and analyzed for the presence of volatile contaminants. If VOCs are detected in the shallow soil gas, the observed compounds may be either in the vadose zone near the probe or in the groundwater below the probe. Since samples are analyzed immediately after they are collected and the findings are available within minutes, the method provides "real-time" results.

Compounds that are good candidates for soil gas analysis exhibit the following general characteristics: low boiling point, low aqueous solubility, high vapor pressures, and favorable resistance to degradation. Thus, soil gas technology is very effective in mapping low molecular weight, halogenated solvent chemicals and petroleum hydrocarbons that possess high vapor pressures and low aqueous solubilities. These compounds readily partition out of the groundwater and into the soil gas as a result of their high gas/liquid partitioning coefficients.

Once in the soil gas, the VOCs diffuse vertically and horizontally through the soil to the ground surface where they dissipate into the atmosphere. Transport of the VOCs in soil gas occurs primarily via gaseous diffusion. Factors affecting this transport include tortuosity of the soil matrix (a measure of the added resistance to diffusion imposed by the structure of the medium), the air filled (drained) porosity of the soil, the gaseous diffusion coefficient of the compound of interest, and the temperature of the soil. Since saturated soils prevent soil gas transport, one of the most important factors to consider when evaluating soil gas survey data is the relationship of soil porosity to saturation.

Because the contamination acts as a source and the aboveground atmosphere acts as a sink, a concentration gradient develops between the two. This concentration gradient between the source and the ground surface may sometimes be distorted by hydrologic and geologic anomalies, such as clays or perched water. Soil gas mapping generally remains effective, however, because the distribution of the contamination is usually broader in areal extent than the local geologic barriers. Also, since many data points are collected during a survey, the contamination is defined by using a large database.

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In other words, the presence of small geologic obstructions may create anomalies in the distribution of the soil gas, but will not obscure the broader areal picture of the configuration of VOCs in the subsurface. For example, trapping VOCs beneath impermeable ground surface covers, such as asphalt parking lots or concrete foundations, normally retards their transport into the atmosphere and increases their concentrations in the shallow soil gas. Investigators, however, can still identify localized "hot spots," or areas of elevated VOC concentrations by simply factoring in this effect when evaluating the data for the entire area.

By gathering meaningful data over a large area in a short period of time, the soil gas investigation saves time and reduces the cost of identifying and locating VOCs in the subsurface. The investigation outlines the general area of contamination much more quickly than the costly conventional method of soil borings and monitoring wells. However, conventional bore holes and observation wells are usually used in concert with the soil gas survey to verify and measure the extent of the contamination.

Soil gas mapping does not replace conventional methodology, but, rather, enhances it by determining the optimum placement of monitoring wells. At the same time, it reduces the likelihood of drilling unnecessary wells. Soil gas surveys rapidly provide data to the site assessor so a superior site investigation can be designed.

### 2.1 EQUIPMENT

Tracer Research utilized an Isuzu analytical van equipped with one GC and two computing integrators. Two built-in gasoline powered generators provided the electrical power (110 volts of alternating current) to operate the gas chromatographic instruments and field equipment. A special hydraulic mechanism consisting of two cylinders and a set of jaws was used to drive and withdraw the sampling probes. When the probes could not be pushed through the subsurface, a hydraulic hammer was used to drive the probes past cobbles and through unusually hard soil.



#### GEOPHYSICAL SURVEY 2.2

Prior to the start of the soil gas investigation, a geophysical survey was conducted. The purpose of the survey was to physically locate the tanks and associated piping as well as any other underground lines in the area. The location of previously marked public utilities were also verified during the survey.

The survey was conducted in the vicinity of the tanks and in the general area where the piping was thought to be located. Radio frequency induction equipment was used to locate the tanks and piping more accurately. The outer edges of the tanks were marked and the piping was traced from the pump back to the tanks and marked with paint. When local geology permitted, ground penetrating radar (GPR) was used to determine the location of underground tanks and plastic piping.

#### SOIL GAS SAMPLING PROCEDURES 2.3

The 7- to 14-foot sampling probes of 3/4-inch diameter hollow steel pipe were fitted with detachable drive tips and advanced 2.5 to 13 feet below ground surface (bgs). The aboveground end of each probe was fitted with an aluminum reducer and a length of polyethylene tubing leading to a vacuum pump. Soil gas was pulled by the vacuum pump into the probe. A vacuum gauge measured the volume of gas pulled into the probe to make sure the flow was adequate.

The volume of air within the probe was purged by evacuating 2 to 5 liters of gas. The evacuation time in minutes versus the vacuum in inches of mercury (Hg) was used to calculate the necessary evacuation time. The vacuum was measured and recorded at each sampling location.

Sample probe vacuums were approximately 2 to 10 inches Hg. The maximum capacity of the pump was approximately 25 inches Hg. This means that if the probe would have become plugged, the vacuum for that particular sampling location would have read 25 inches Hg.

During the soil gas evacuation, samples were collected in a glass syringe by inserting a syringe needle through a silicone rubber segment in the evacuation line and down into the steel probe. Up to 10 milliliters (mL) of soil gas sample was collected for immediate analysis in the Tracer Research analytical van. Subsamples (replicate injections)

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of soil gas were injected into the GC in volumes ranging from 1 to 1,000 microliters, depending on the VOC concentration at each location.

### 2.4 GROUNDWATER SAMPLING PROCEDURES

If groundwater was encountered at any depth during the collection of soil gas samples, a groundwater sample was collected for analysis. The hollow 3/4-inch probes, 7-to 14-feet in length, with detachable drive points were driven below the water table. The groundwater samples were collected at a depth of 3 to 12 feet bgs. Once at the desired depth, the probes were withdrawn several inches to permit water to flow into the resulting holes. After insertion into the ground, the aboveground end of the sampling probes were fitted with a vacuum adaptor (metal reducer) and a length of polyethylene tubing leading to a vacuum pump. A vacuum of up to 25 inches of mercury was applied to the interior of the probe for 10 to 15 minutes, or until water was drawn up the probe. The water thus accumulated was removed by drawing a vacuum on a 1/4-inch polyethylene tube inserted down the probe to the bottom of the open hole. Because the water was induced to flow into a very narrow hole, it was sampled with little exposure to air and, consequently, there was little loss of volatile compounds by evaporation. The polyethylene tubing was used once and discarded to avoid cross contamination.

The groundwater samples were collected in 40 milliliter (mL) VOA vials that were filled to exclude air and then capped with a Teflon-lined septa cap. Approximately half of the liquid in the bottle was decanted, the vial was shaken vigorously, and a sample of the headspace from the container was injected into the GC.

Indirect (headspace) analysis is the preferred technique when a large number of water samples are to be performed daily. The method is more time efficient for the measurement of volatile organics than direct injection of the water sample into the GC because there is less chance of semi-volatile and non-volatile organics contaminating the system. Depending upon the partitioning coefficient of a given compound, the indirect analysis method may be more sensitive than the direct injection method of analysis. The precision and accuracy of both methods are similar.

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### 2.5 ANALYTICAL PROCEDURES

A Hewlett Packard 5890 Series II gas chromatograph was used for the soil gas and groundwater sample analyses. Compounds were separated in the GC on a 4-foot by 1/8-inch outer diameter (OD) packed analytical column (10% TCEP as the stationary phase bonded to Chromosorb PAW support) in a temperature controlled oven. Nitrogen was used as the carrier gas.

#### GC Process

The groundwater headspace vapor and the soil gas samples are injected into the GC where the vapor is swept through the analytical column by the carrier gas. The detector senses the presence of a component different from the carrier gas and converts that information to an electrical signal. Because the components of the sample pass through the column at different rates, according to their individual boiling point, and are detected as they leave the FID, they are identified by the time it takes them to pass through the column.

### FID Process

The FID utilizes a flame produced by the combustion of hydrogen and air. When a component, which has been separated on the GC analytical column, is introduced into the flame, a large increase in ions occurs. A polarizing voltage is applied to an ion collector near the flame. The ions are attracted to the collector, producing a current which is proportional to the amount of the sample analyte in the flame. The electrical current causes the computing integrator to record a peak on the chromatogram. By measuring the area of the peak and comparing that area to the integrator response of a known aqueous standard, the concentration of the analyte in the sample is determined.

#### **Detection Limits**

Detection limits depend on the volume of the injection as well as the sensitivity of the detector to the individual compound. Generally, the larger the injection size, the greater the sensitivity. However, the peaks for target compounds had to be kept within the linear and operating ranges of the analytical equipment.



If target compounds are present at high concentrations it may be necessary to dilute the sample or to decrease the volume of the injection in order to measure the compound's peak on the chromatogram. This sometimes causes decreased detection of other target compounds. Consequently, for optimum detection limits, it is necessary to analyze the largest sample possible while staying within the operating and linear ranges of the equipment. For these reasons, Tracer Research may perform several injections for each sample collected.

The detection limits of the target compounds were calculated from the response factor, the sample size, and the calculated minimum peak size (area) observed under the conditions of the analysis. The limits of the hydrocarbon compounds were approximately 0.1 micrograms per liter ( $\mu$ g/L). If any compound was not detected, the detection limit for that compound in that analysis was given as a "less than" value, e.g., <0.1 ug/L.

# 2.6 QUALITY ASSURANCE AND QUALITY CONTROL

Tracer Research's Quality Assurance (QA) and Quality Control (QC) program was followed to maintain data that was reproducible through the investigation. An overview presenting the significant aspects of this program is presented below.

# Soil Gas/Groundwater Sampling Quality Assurance

To ensure consistent collection of samples, the following procedures are performed:

### - Sampling Manifolds

Tracer Research's custom designed sampling manifold connects the sample probe to the vacuum line and pump. The manifold is designed to eliminate sample exposure to the polymeric (plastic) materials that connect the probe to the vacuum pump.

The sampling manifold attaches to the end of the probe, forming an air tight union between the probe and the silicon tubing septum. The septum connects the manifold to the pump vacuum line and permits syringe sampling.



This sampling system allows the sample to be taken upstream of the sampling pump, manifold, and septum. Since cross contamination of sampling equipment can be a major problem, Tracer Research replaces the materials (probe and syringe) that contact the soil gas before or during sampling.

### -Sampling Probes

Steel probes are used only once each day. To eliminate the possibility of cross contamination, they are washed with high pressure soap and hot water spray, or steam-cleaned. Enough sampling probes are carried on each van to avoid the need to re-use any during the day.

### -Glass Syringes

Glass syringes are used for only one sample a day and are washed and baked out at night. If they must be used twice, they are purged with carrier gas (nitrogen) and baked out between probe samplings.

## - Polyethylene Tubing and VOA Vials

Polyetheylene tubing and VOA vials used for the collection of groundwater samples are used only once and then discarded to avoid cross contamination.

## -Sampling Efficiency

Soil gas/groundwater pumping is monitored by a vacuum gauge to ensure that an adequate flow of gas/water from the soil is maintained. A reliable gas sample can be obtained if the sample vacuum gauge reading is at least 2 inches Hg less than the maximum measured vacuum of the vacuum pump.

# Analytical Quality Assurance Samples

Quality assurance samples are performed as shown in Table 1 at the listed, or greater, frequencies. The frequency depends on the number of soil gas/groundwater samples analyzed and the length of time of the survey.



Table 1. Quality Assurance Samples

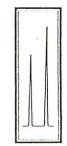
Sample type	Frequency
Ambient Air Samples	2 per day or 1 per site
Analytical Method Blanks	1 per day
Continuing Calibration Check	20% (1 every 5 samples)
Field System Blank	1 per day
Reagent Blank	1 per set of working standards
Replicate Samples	10% of all samples

The ambient air samples are obtained on site by sampling the air immediately outside the mobile analytical van and directly injecting it into the GC. Analytical method blanks are taken to demonstrate that the analytical instrumentation is not contaminated. These are performed by injecting carrier gas (nitrogen) into the GC with the sampling syringe. Subsampling syringes are also checked in this fashion.

The injector port septa through which samples are injected into the GC are replaced daily to prevent possible gas leaks from the chromatographic column. All sampling and subsampling syringes are decontaminated after use and are not used again until they have been decontaminated by washing in anionic detergent and baking at 90°C.

Field system blanks are analyzed to check for contamination of the sampling apparatus, e.g., probe and sampling syringe. A sample is collected using standard soil gas sampling procedures, but without putting the probe into the ground. The results are compared to those obtained from a concurrently sampled ambient air analysis.

If the blanks detect compounds of interest at concentrations that indicate equipment contamination or concentrations that exceed normal background levels (ambient air analysis), corrective actions are performed. If the problem cannot be corrected, an out-of-control event is documented and reported.



A reagent blank is performed to ensure the solvent used to dilute the stock standards is not contaminated. Analytical instruments are calibrated daily using fresh working standards made from National Institute of Sciences and Technology traceable standards and reagent blanked solvents.

Quantitative precision is assured by replicating analysis of 10 percent of all samples. Replicate analyses are performed by subsampling vapors from the original sampling syringe or VOA.

#### TEST RESULTS 3.0

Prior to the start of the investigation, preliminary sampling locations were determined by Idaho Petroleum Storage Tank Fund personnel. Condensed data is included in Appendix A. A map view of the site showing the sampling locations and TVHC contours is presented in Appendix B.

Fourteen soil gas and five groundwater samples were collected from twelve locations and analyzed. TVHC detected in the soil gas ranged from 2 to  $51,000 \mu g/L$ (SG-1-4'). TVHC in the groundwater ranged from 450 to 3,200,000  $\mu$ g/L (WS-5-12'). TVHC were greater than 1,000 µg/L at six locations.

Benzene, toluene, ethyl benzene and xylenes were also detected at this site. Benzene concentrations ranged from 0.06 μg/L to 310 μg/L (SG-1-4') in the soil gas and from 6  $\mu$ g/L to 120,000  $\mu$ g/L in the shallow groundwater. Toluene was detected at eight locations. Ethylbenzene concentrations ranged from 6 µg/L to 80 µg/L in the soil gas and from 4 µg/L to 18,000 µg/L in the shallow groundwater. The highest concentration of xylenes in the soil gas was detected at location SG-11-3' (600 μg/L). Xylenes ranged from 44 to 230,000 μg/L in the shallow groundwater.

Plummer Quik Stop/Plummer, Idaho/IPSTF/IPSTF No. 1430-5-2/Job No. 1150020S TRACER RESEARCH CORPORATION - ANALYTICAL RESULTS

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